Microwave Curing of Non-Traditional Polymer Materials Used in Manufacture of Injection Moulds

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Abstract

Microwave heating technology is a cost-effective alternative way for heating and curing of used in polymer processing of various alternate materials. The work presented in this paper addresses the attempts made by the authors to study the glass transition temperature and curing of materials such as casting resins R2512, R2515 and laminating resin GPR 2516 in combination with two hardeners ADH 2403 and ADH 2409. The magnetron microwave generator used in this research is operating at a frequency of 2.45 GHz with a hollow rectangular waveguide. During this investigation it has been noted that microwave heated mould materials resulted with higher glass transition temperatures and better microstructure. It also noted that Microwave curing resulted in a shorter curing time to reach the maximum percentage cure. From this study it can be concluded that microwave technology can be efficiently and effectively used to cure new generation alternate polymer materials for manufacture of injection moulds in a rapid and efficient manner. Microwave curing resulted in a shorter curing time to reach the maximum percentage cure.

Introduction

Epoxy resins are gaining popularity in various field of engineering, such as in the electrical industry, for structural applications in both the commercial and military aircraft industries.
At present, the most common curing technique for epoxy resin is by conventional oven curing and it takes prolonged period of time. This leads to study of alternate curing technique by using microwave heating, which is expected to shorten the curing period. Microwave technology is being adopted in industries working on the major principle of volumetric heating and releases heat to cure a wide range of materials. At present this technology is used in the curing of polymers, but, in the past decade, various studies and interests have been focused on implementing microwave curing of other materials with a different molecular setup. Therefore, this proposed research would only concentrate on the curing of alternative mould materials by using microwave heating.

Theory

Microwaves are electromagnetic waves with wavelengths ranging from 1 mm to 1 m and frequency that ranges from 300 MHz to 30 GHz. According to international agreement, industrial microwaves operate at a frequency of 2.54 GHz, which is powered by a variable power generator up to 1.26kW. The microwave oven uses a magnetron to create intense microwaves that are channeled to the microwave cavity using electromagnetic waves with a frequency of 2.45 GHz. However, if greater power penetration is required, a system with a frequency of 915 MHz can be used. Important properties that are involved in the theory of microwave curing of materials include the

wave propagation, microwave instrumentation (which includes the magnetron, impedance matching and tuning, waveguides used and the microwave cavity) and the dielectric properties of the material. The heating pattern of a sample that is heated by microwaves will depend on the dissipation factor which can be expressed by Eq (1) and the dielectric may be assumed to have a complex dielectric constant as shown in Eq. (2)

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \quad (1)$$

$$\epsilon = \epsilon' + j\epsilon'' \quad (2)$$

The energy that is absorbed by the sample as the microwave energy penetrates and is dependent on the sample's dissipation factor. Materials that are transparent to microwave energy, penetration is considered to be infinite. As in the case of reflective materials such as metals, penetration is considered to be zero. However, the dissipation factors for absorptive materials are finite.

Background and Literature Review

The applications of microwave heating have been recently gaining more and more visibility and have been successfully used in the food, automobile, rubber and other processing industries. The microwaves are used to pre-heat rubber rapidly and uniformly before placing it in a conventional oven to shorten the final curing time. Based on their previous research [1,2] the authors cited that microwaves could interact with materials by both the polarization or conduction process. For polarization to occur, the build up and decay of the electric field occurs at a high frequency. Due to this, energy is converted from electrical field to stored potential energy. The stored potential energy is then converted to store random kinetic or thermal energy in the material. Dielectric losses are due to ionic conduction and polarization, which occurs mainly at low and high frequencies respectively. Number of researchers [3] studied the applications of microwave heating in different disciplines of engineering. In their work Clark et al. [4] reviewed the research conducted by many researchers in the field of microwave processing and other related applications. In addition, they discussed microwave processing examples such as polymer curing. Processing of both polymers and polymer composites are done using microwaves. For certain epoxies, a pulsed microwave would result in a higher polymerization rate, uniformed Yarlagadda and Chong [1] studied the behavior of ceramics when joined by using microwave heating technique. Boey and Yap [5] studied the effects of curing agents on the glass transition temperature. They cured diglycidyl ether of bisphenol-A (DGEBA) and used three curing agents, namely diaminodiphenylsulfone (DDS), diaminodipheriylmethane (DDM) and *meta*-phenylene diamine (MPDA). Their results have shown that the three curing agents caused DGEBA to cure at a faster rate in microwave curing compared with the conventional curing process. They concluded that by using microwave curing, the maximum values of percentage cure and glass transition temperature are much lower than those of thermal curing [5]. Wei et al. [6] also researched by comparing microwave and thermal curing of epoxy resins. They also did studies of DGEBA with two different curing agents, DDS and mPDA. The experiments were carried out by both microwave and thermal curing with thin film samples acquired. Their results clearly indicate that microwave curing increases reaction rates compared with thermal curing [6]. Olofinjana et al. [2] studied the microwave processing of adhesive joints using a temperature-controlled feedback system. Their results indicated that curing of epoxies using microwaves reduces curing time and could improve the mechanical properties. They concluded that it is necessary to have precise temperature control in order to prevent material damage; in their work they compared bond strengths of epoxies cured by microwaves versus samples cured via ambient temperatures. Their results clearly shown that epoxies cured by microwaves have higher bond strength as compared to ambient curing. In their research Jacob et al. [7] developed process models based on microwave-induced reaction. From their work they demonstrated that the rate of cross-linking of epoxy

materials (DGEBA and DDS) was much higher in microwave curing compared to conventional curing. As indicated the glass transition temperature (*T*g) was obtained within 13–20 min by microwave cure as compared to 4 h with conventional cure. Nightingale and Day [8] studied various curing procedures that includes autoclave curing, microwave post-curing and full microwave curing [12-14]. From their study they concluded that the longest post-curing that took place was 20 min.

In the proposed research attempts have been made to study various mechanical properties such as tensile strength, Rockwell hardness, fracture surface of microwave cured materials and to analyze the glass transition temperature (*T*g) of epoxy resins with microwave-oven-cured and finally to analyse the microstructure of epoxy resins cured with microwave curing techniques.

Experimental Facility Used

A magnetron as shown in Fig. 1 is used to generate intense electromagnetic waves with a frequency of 2.45 GHz. This 2.45 GHz magnetron tube is one of the most commonly used tubes in the industry. The microwave generator that is used has digital displays, which outputs the forwarded and reflected wave power that could be adjusted by a dial on the microwave generator. The stub tuners Fig. 1c are used for the impedance matching for the unnecessary loss of power or the tuning of the microwave system. Impedance matching is required to minimise the reflectance of the travelling waves travelling from one medium to another. Ideally, the system would be perfectly matched if the microwaves that travel from the magnetron to the sample in the microwave cavity are not reflected back. However in many cases, mismatching occurs. Tuners are used for impedance matching to provide the maximum absorption and minimise the reflected power back to the magnetron. This is important as the reflected microwaves could cause the magnetron to overheat excessively and change the output of the magnetron. The absence of an absorber in the cavity will also increase any minor leakage of microwaves from the system because the microwave intensity inside the cavity will be much higher than normal. The waveguide Fig. 1 is a device that channels the microwaves generated by the magnetron to the cavity with little loss and virtually no leakage hazard. There are many cross sectional shapes of waveguides available. Cross sections of almost any shape can be used. However, the analysis of odd shaped cross sections would prove to be difficult. Round cross sectional waveguides are rather common.

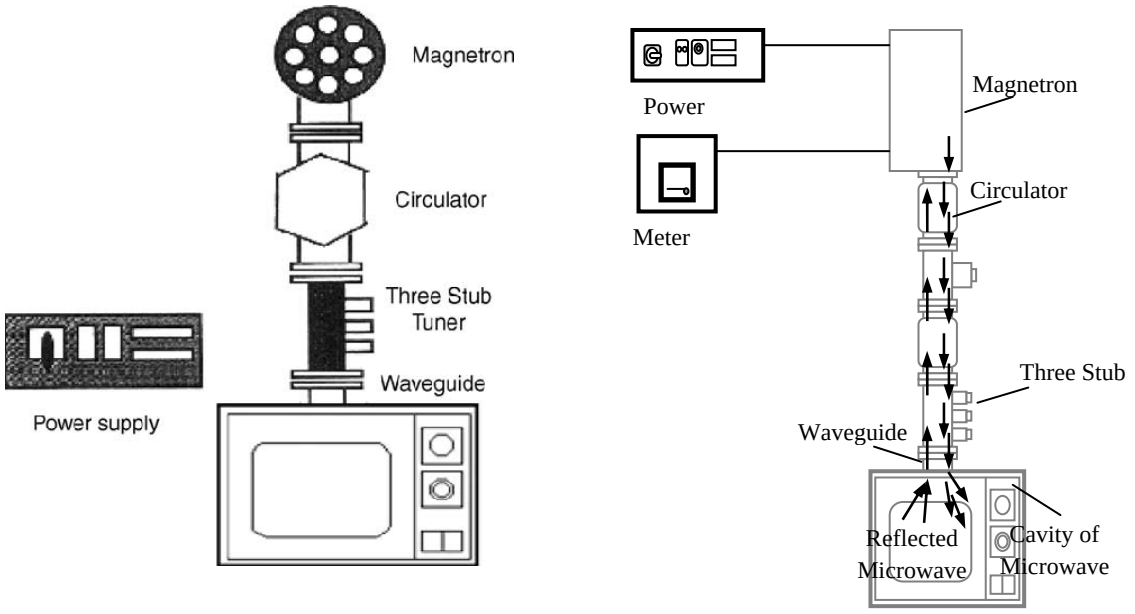

Fig.1 Schematic Drawing and Microwave Setup used for Curing of Mould Materials

Differential scanning calorimetry is a known technique, used to measure the glass transition temperature of cured materials. In this study, TA Instruments Q100 was used to perform this task. The principle used in DSC is to measure the difference between the heat flow to a sample with reference to another sample, under reference conditions of time and temperature. Both testing sample and reference sample are heated together in the furnace with the same source and the measurement of temperature difference (ΔT) is taken. The signal of ΔT is then converted to a power difference ΔP by using the calorimetric sensitivity [10]. Scanning electron microscopy is used to study the fractured surfaces. Fractured surface obtained from mechanical tests were examined at various magnifications by using FEI Quanta 200 microscope in order to observe the fracture behaviour of the specimens. Hull [11] described the principle of SEM as the fracture surface is scanned, on a rectangular or square raster, by a finely focused beam of high-energy electrons (typically 5–40 keV). The electrons penetrate the surface of the specimen and interact with the atoms of the material in a variety of elastic and inelastic scattering processes. Scattering continues until either the electrons escape from the specimen or are absorbed by the material [11].

In addition a second set of equipment was used for the testing of material properties like tensile strength, flexural strength and hardness tests were conducted. In addition, tests to find the glass transition temperature of the materials were also conducted and the morphology of the fracture surface were studied. The test method uses the theory of a three point load acting on a simply support beam. There are mainly two procedures of testing the flexural properties as stated in the ASTM D 790-00 Standards. At least five specimens for mould materials have to be done with a recommended specimen size of 127 mm x 12.7 mm x 3.2 mm. They are then placed on a three point support jig that utilises the Hounsfield machine. As recommended, a support span-to-depth ratio of 16:1 has to be used unless specified. The fracture surface of the specimens measured by coating the specimen with a conductive material since it is very difficult to record scanning electronic microscopy photographs due to specimen's charging effects.

Materials investigated

After careful consideration and analysing issues from the development of mould materials point of view three commercially used epoxy resins, two different speeds of hardeners, anti-sag agent and filler were used in the proposed study. The technical data and other scientific information of the three chosen epoxy resins and two different speeds of hardeners used are given in Table 1. Fillers are commonly added into the mixed solution of epoxy resins and hardeners to change or improve the physical, mechanical and processing properties. One of the best examples is calcium sulphate which is used to increase impact, tensile and compressive strength [9]. Alternatively, large amount of fillers can also be used to decrease the amount of epoxy resins used in order to reduce the cost of epoxy resins. In this case, aluminium hydrate ($Al(OH)_3$ or ATH) was chosen as filler and as purpose to retard the flammability [3]. Another material, aerosil, was chosen as an anti-sag agent since huge amount of fillers caused the high density and may lead to non-uniform curing.

Table 1: Technical data of Epoxy resins and Hardeners used in this study

Product	**Chemical Name**	**Application**
GPR2512	Bisphenol-A-based epoxy resin	A casting resin for fabrication of foundry patterns
GPR2515	Bisphenol-A-based epoxy resin	For tools required to operate at high temperatures
GPR2516	Bisphenol-A-based epoxy resin	For general laminating applications
ADH 2403	Isophorone diamine	Tooling hardener high temperature—fast
ADH2409	Cyclohexylamine	Casting hardener high temperature—slow

Results & Discussions

Tensile tests were done and the final mean results for each specimen at typical room temperatures were tabulated in Table 2. From the results shown, the three different materials exhibit tensile strengths of different values. In general, out of the three epoxy resins tested, results on the tensile strength properties of the microwave cured unreinforced epoxy resins shows rather encouraging results. However for the case of Resin R2515, results proved to be unsatisfactory and were found to be rather brittle. Another important factor in the tensile properties of the material is it's percentage elongation. The values tabulated in Table 2 shows in general that resin R 2515 experiences very little elongation before it fails as compared to resins R 2512 and R 2516. In general, resin R 2515 is considered to be a brittle resin as is exhibits very little plastic deformation upon fracture. As compared to certain materials like metals, epoxies are not as ductile. Flexural strength tests are carried out on the proposed sample to find out the ability of the specimens to resist deformation under a load. Results of the flexural strength tests are shown in Table 2. For specimens that do not break, the load at yield, typically measured at 5% deformation/strain of the outer surface, is reported as the flexural strength. As the results show, resin R 2515 is a rather brittle resin which exhibits low flexural strength. Resin R 2516 gives an overall tougher flexural strength and has a greater ability to resist deformation.

The higher the Rockwell hardness number, the harder the material is. From the results shown in Table 2, it can be seen that resin R 2515 is of a harder material as compared to the other two. R 2516 is also harder than resin R 2512. The results obtained from this test are a useful measure of relative resistance to indentation of various grades of plastics. However, the Rockwell hardness test does not serve well as a predictor of other properties such as strength or resistance to scratches, abrasion, or wear, and should not be used alone for product design specifications.

Table 2: Tabulated results for various mechanical properties studied with microwave curing

Specimen	Tensile Strength (MPa)	Percentage Elongation (%)	Flexural Strength (MPa)	Rockwell Hardness Number (HRE)
R 2512 / H 2403	46	3.21	167	57
R 2512 / H 2409	28	2.54	135	58
R 2515 / H 2403	15	1.04	70	60
R 2515 / H 2409	12	1.14	17	63
R 2516 / H 2403	45	3.25	177	58
R 2516 / H 2409	50	3.32	145	60

Glass Transition Temperature Comparisons between Conventionally cured and Microwave Cured Mould Materials

Glass transition temperature (*T*g) indicates the point at which the material changes from glass to rubber. Below *T*g, the molecules inside of material do not have enough energy to rearrange or rotate themselves, thus it is relatively brittle so it is a glass. Once the material is heated up to *T*g, the molecules start cross-linking and become more mobile due to the heat capacity increase. At this point, the material exhibits rubbery properties [10]. It is necessary to perform the *T*g test since the mechanical strength decreases rapidly once the material passes this transition. In this experiment, samples for both microwave and conventional cured were tested to show which curing technique

gives higher glass transition temperature. Under the conventional DSC, the heat flow has a cyclic component which is made up of the sine and cosine term, the amplitude of which is determined by a Fourier transform analysis. The Glass Transition Temperature test was done to compare if samples cured by microwave improves the material's Glass Transition Temperature. The results shown in Table 3 show improvement in the Glass Transition temperature as compared to the epoxy resins cured using the conventional oven.

Table 3: Tabulated Results for Glass Transition Temperatures

Specimen	Microwave Oven	Conventional Oven
R 2512 / H 2409	80.22	71.74
R 2515 / H 2409	86.06	54.04
R 2516 / H 2409	85.92	78.30

In general, the T_g for resin R 2512 has increased an average of 11.82%, resin R 2515 experiences and increase of 59.25% and T_g for resin R 2516 has improved by 9.73%. It is therefore important to increase the material's Glass Transition temperature, so as to have a general increase in the temperature where the material starts to degrade. This is important as the material would then perform and would not fail in higher temperatures as compared to the same material with a low T_g.

Fracture Surface Microstructure Analysis by SEM

The fracture surface of Resin and Hardener Mix R 2512 / H 2403 were observed under a magnification of 76 times. The overall surface exhibits a rather smooth texture. In Fig. 2, bowed-out crack fronts and trailing river lines can be seen. The river lines are on cleavage cracks of the fracture surface. Splinters or filaments of material that have separated at the steps and lie at random angles on the surface are also observed. Dust specks can bee seen on the fracture surface which could be due to dust particles in the air or filaments of material that have landed on the fracture surface. The fracture surface of R 2512 / H 2409 in Fig. 3 shows a progressive increase in roughness. The crack propagated from the edge and the difference on the fracture surface could be due to compression on one end and tension on the other. Closer examination of the surface shows that river lines and terraces cover particular section of the fracture surface.

Fig. 4 of mixture R 2515 / H 2403 shows various cracks nucleated at the void defect due to high tensile stress. Certain areas of the fracture surface also show steps that form as the crack propagates through the material and the area near the void shows faceted curved surfaces and river patterns. The reason for this fracture surface shape could be due to the reason that the material was bent forward and backwards before fracture occurs. The fracture surface of epoxy resin R 2515 / H 2409 shows various defects and formations of cracks. Fig. 5 shows an example of a "stop-go" crack with a re-initiation point. Markings of "speed oscillating" cracks can also be observed. Chip marks can also be seen which could be formed by an indention of an object on the surface of the material.

Bubbles, voids and cracks can be seen on this fracture surface in Fig.6 and overall, the fracture surface has a clean fracture. These results shows that resin mixture of R 2515 / H 2409 is of a rather brittle nature. Fracture surface of resin mix R 2516 / H 2403 exhibits a rather cleavaged fracture. Further observations show river step cleavage cracks forming and ridges form perpendicular to the direction of crack growth. Bubbles shown in the SEM picture are of two shades. The lighter shaded bubbles are closer to the fracture surface while the darker bubbles formed are deeper inside the material. From the fracture surface shown, the direction of the crack propagation can be seen and this material is rather tough and resilient.

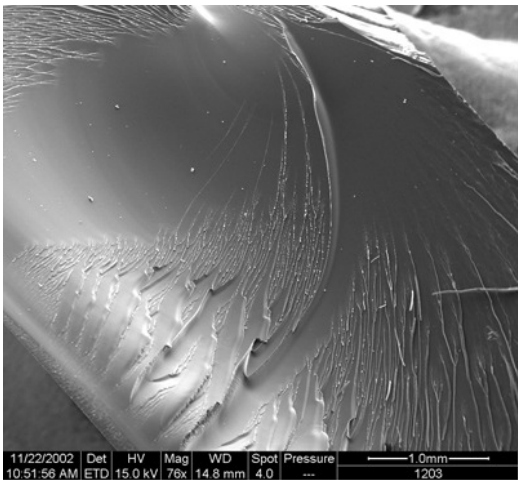

Fig2: SEM Image of R 2512 / H 2403

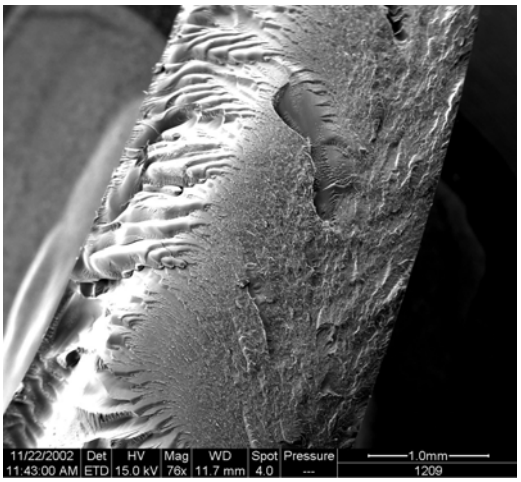

Fig 3: SEM Image of R 2512 / H 2409

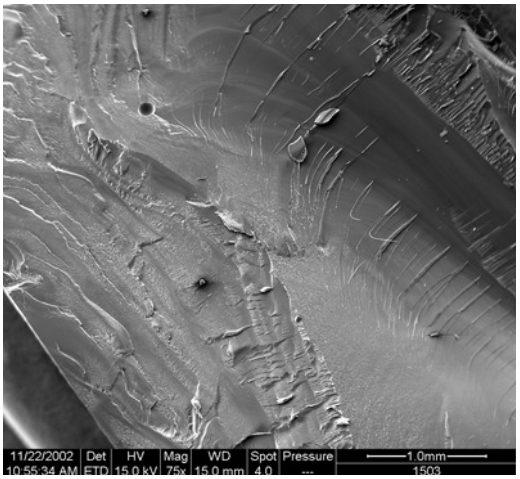

Fig 4: SEM Image of R 2515 / H 2403

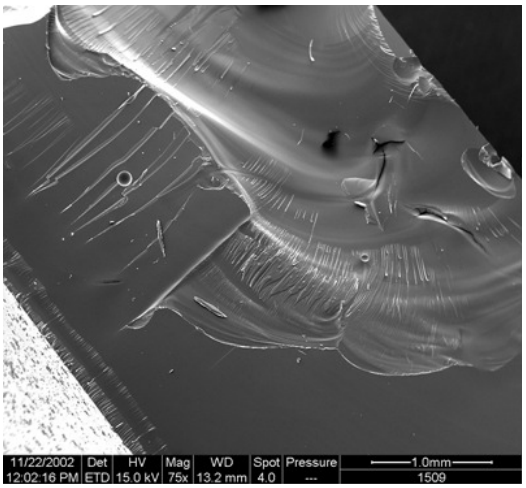

Fig 5: SEM Image of R 2515 / H 2409

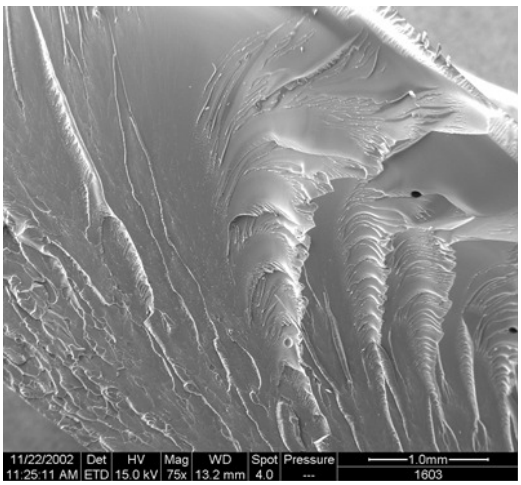

Fig 6: SEM Image of R 2516 / H 2403

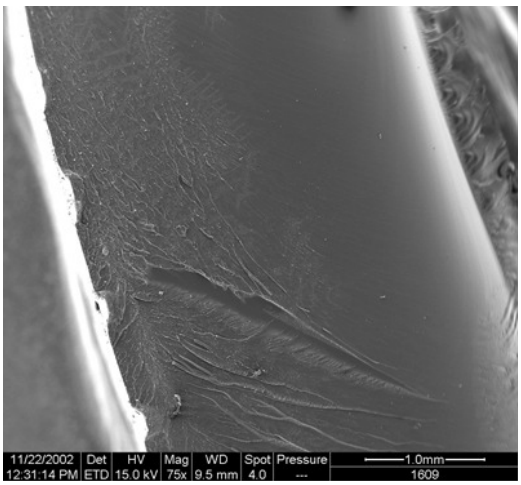

Fig 7: SEM Image of R 2516 / H 2409

Fig. 7 shows how the material fails and rough surfaces that form due to stresses involves as it propagates through the crack. Further observation shows a permanent slip band crack produced by alternating stresses. The direction of the crack propagation could also be seen as the fracture surface starts of smooth and ends up rough. The material is rather tough however gives a clean fracture surface.

Conclusion

In this work attempts have been made by the authors to study the affects of microwave curing of epoxy resins for development of alternate mould materials. The ability of using microwave energy to cure alternate un-reinforced mould materials were investigated. Initially, it can be seen from the fracture surfaces obtained by using the SEM that there are a large number of cavities present. This indicates that the preparation of the solution for the resin was not satisfactory. The occurrence of cavities in the specimen would increase the possibility of rupture while subjected to loading. The accuracy of the results of the tensile test could be improved by further refining the process of preparing the samples. This clearly indicates that microwave curing has the capacity to improve the strength of the samples better than the samples cured through conventional heating. Finally, the results for the glass transition temperature for microwave-cured samples showed an increase in glass transition temperature when compared to conventional-cured samples. As the materials will degrade once the temperature exceeds the transition temperature, it is important that the glass transition temperature is as high as possible and from the present study it is evident that microwave curing of epoxy resins will improve glass transition temperature, which is a desirable feature for development of efficient and alternative mould materials.

Satisfactory results were obtained on all three alternate mould materials were researched on. However, the process of moulding and it's materials go far beyond than just casting. The effects on using microwave heating to develop and cure the mould materials clearly shows a great improvement in the time taken to cure. Material properties were not greatly affected with the exception of Resin R 2515 which turned out to be very brittle even after reaching it's "C state". In general, comparing both the results of the time taken to cure mould materials with the use of microwave heating has improved tremendously and could increase the overall productivity of productions. However, further research has to be done on the feasibility of implementing microwave heating to be used in the industry. This is due to certain factors, which include high capital cost, not well understood by the industrial community and most importantly, a microwave system has to be customised for a certain moulding process that is involved.

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References

[1] P.K.D.V. Yarlagadda, T.S. Chong, Characterisation of materials behaviour in microwave joining of ceramics, J. Mater. Process. Technol. 84 (1998) 162–174.

[2] A. Olofinjana, P.K.D.V. Yarlagadda, A. Oloyede, Microwave processing of adhesive joints using a temperature controlled feedback system, Int. J. Machine Tools Manuf. 41 (2001) 209–225.

[3] Solid Surface 2001, ATH—filler with an attitude. URL:http://www.solidsurfacemagazine.com/mar 2001.htm.

[4] P.K.D.V. Yarlagadda, A. Ahmed, C.T. Soon, E. Siorgs, Microwave welding of alumina ceramic using a ridge wave guide, in: D.E.Clark, W.H. Sutton, D.A. Lewis (Eds.), Proceedings of the First World Congress on Microwave Processing; Ceram. Trans. 80 (1997) 475–482.

[5] F.Y.C. Boey, B.H. Yap, Microwave curing of an epoxy-amine system: effect of curing agent on the glass-transition temperature, Polym. Test. 20 (2001) 837–845.

[6] J. Wei, M.C. Hawley, J.D. Delong, Comparison of microwave and thermal cure of epoxy resins, Polym. Eng. Sci. 33 (17) (1993) 1132– 1140.

[7] J. Jacob, L.H.L. Chin, F.Y.C. Boey, Thermal and non-thermal interaction of microwave radiation with materials, J. Mater. Sci. 30 (1995) 5321–5327.

[8] C. Nightingale, R.J. Day, Flexural and inter-laminar shear strength properties of carbon fibre/epoxy composites cured thermally and with microwave radiation, Compos. A: Appl. Sci. Manuf. 33 (7) (2002) 1021–1030.

[9] P.L. Mangonon, The Principles of Materials Selection for Engineering Design, Prentice-Hall, New Jersey, 1999.

[10] P.J. Haines, Thermal Methods of Analysis Principles, Applications and Problems, Blackie Academic and Professional, UK, 1995.

[11] D. Hull, Fractography: Observing, Measuring and Interpreting Fracture Surface Topography, The press Syndicate of the University of Cambridge, UK, 1999.

[12] D. Boghdal, P. Penczek, J. Pielichowski and A. Prociak, Microwave assisted sy6nthesis, crosslinking and processing of polymeric materials, Advances in Polymer Sciences, 2003, 163 (2003) 51-58.

[13] T. Chaowasakoo and N. Sombatsompop**,** Mechanical and morphological properties of fly ash/epoxy composites using conventional thermal and microwave curing methods, Composites Science and Technology, 67 (2007), 2282-2291.

[14] T.Tilford, C. Bailey, M.P.Y. Desmulliez, G. Goussettis, A.K. Parrott and A.J. Sangster, Multiphysicis simulation of microwave curing in micro-electronics packaging applications, Soldering and Surface Mount Technology, 19 (2007)